

METHOD OF IMPROVING THE PERFORMANCE OF ORGANIC COATINGS
FOR CORROSION RESISTANCE

FIELD OF THE INVENTION

This invention applies to polymeric resins that are used to coat metallic substrates for corrosion protection, and to a method of modifying the resins with organosulfur compounds for improved corrosion resistance. In particular, the invention pertains to preparing a homogeneous mixture of the resin and the organosulfur compound.

BACKGROUND OF THE INVENTION

Metals that are exposed to the ambient for prolonged periods of time require coatings to protect the exposed surface from corrosion. Steel producers use various organic and inorganic coatings to protect cold-rolled steel (CRS) sheets from corrosion during shipment and storage. The common practice in providing temporary corrosion protection for steel sheets is to apply a conversion coating. Traditionally, conversion coatings are produced by exposing untreated or galvanized CRS sheets to phosphoric acid or chromic acid treatment or both. The latter provides the most effective corrosion protection. However, increased environmental and safety concerns on the use of chrome have generated strong interest in developing chrome-free conversion coatings. Most of the new developments are based on replacing chromation with organic coatings.

It is well known that coating steel with a resin solution containing an organosilane coupling agent provides corrosion protection. Woo, et al. (U.S. patent No. 5,077,354) disclosed a method of mixing a silicon resin with ethylenically unsaturated monomers in a solvent, heating the solution to 50-150°C, and agitating the solution until polymerization is complete. According to van Ooij (U.S. patent No. 5,455,080), this method suffers from the weak bonding between the paint and steel substrate. The reason is that silicone resin has already been reacted with the ethylenic monomers when forming the acrylic polymer, which in turn prevents the silicon resin from acting as a coupling agent between the outer acrylic layer and the steel substrate.

Van Ooij, et al. (U.S. patents 5,455,080; 5,498,481; 5,539,031) disclosed methods of coating CRS or electrogalvanized (EG) steel with a blended powder

mixture comprising a thermosetting resin, a pigment and non-hydrolyzed organosilane coupling agent. The mixture contains 0.01–10% by weight of an organosilane whose melting temperature is lower than the curing temperature of the resin. It is believed that organosilanes can diffuse toward a metal surface and form a crosslinked layer during curing step.

Purnel, et al. (U.S. patent 5,389,405) and Morris, et al. (U.S. patent 5,412,011) disclosed chromium-free conversion coatings for metal surfaces such as aluminum, steel, and galvanized steel, which are applied on the surfaces as aqueous solutions of anionic polyacrylamide copolymer, inorganic silicate, and organofunctional silane.

There have been a few attempts to incorporate surfactants into polymer or other coatings to increase corrosion resistance. Sankaranaryanan and Subbaiyan (1993) added 1g/l octadecyl dithiocarbamate ($C_{18}H_{37}NHCSSH$) to a phosphating bath to improve the corrosion resistance of phosphated steel. Van Alsten (1999) added 1,000 ppm of an alkyl bis-phosphonic acid and zinc acetate to an ethylene and methacrylic acid copolymer. The mixture is melt-pressed onto CRS panels to form a film of approximately 2 mm in thickness. The film was subsequently cured in a vacuum oven at 150°C to allow for the surfactant (i.e., octadecyl dithiocarbamate) to form self-assembled monolayers (SAMs). Although the process of forming SAMs from a rather thick polymer melt was sluggish, using alkyl bis-phosphonic acid and zinc acetate as additives to polymeric resin improved the coating properties after several minutes of annealing time.

Shimakura, et al. (EP 1,002,889) disclosed an anticorrosive coating composition, comprising a silane coupling agent and an aqueous resin solution (or suspension). Additionally, phosphorus-containing ions and/or sulfur-containing compounds can be added to the coating solution. The sulfur-containing compounds disclosed in this invention may be selected from the groups consisting of thio-carbonyls, triazine thiols, sulfide ions, and persulfate ions.

Kanai and Shimakura (U.S. patent 6,607,587) disclosed an anticorrosive coating for metals, which comprises a resin, water, water-dispersible silica, and a thio-carbonyl compound.

Organosulfur compounds have a strong affinity for metal substrates and can

form close packed SAMs on the surface. There have been attempts to use this SAMs to produce a corrosion-resistant coating (Jenning, 1996; Nozawa, 1997; Aramaki, 1999; Taneichi, 2001). The invention described herein uses sulfur-containing organic compounds to modify resin solutions for forming a durable coating with enhanced corrosion resistance.

SUMMARY OF THE INVENTION

The instant invention describes a method of improving the performance of organic conversion coatings for metals by modifying the compositions of the organic resins by adding an organosulfur compounds. The improved performance of the modified resin compositions can protect metal substrates from corrosion without chromation. Several possible mechanisms may operate to enhance the properties of the coating:

i) The sulfur-containing surfactants disclosed in the instant invention chemisorb on the surfaces of the metallic substrates, and give rise to improved adhesion of the organic resins on the substrates.

ii) The surface free energies of the metallic substrates are reduced and, therefore, render the substrates less susceptible to corrosion.

iii) The small organosulfur compounds as compared to the molecules of the resins can readily fill the pores of polymer matrix, thereby increasing the barrier effect for corrosion protection.

iv) The organosulfur compounds of the invention may be more readily oxidized than the substrates, thereby serving as anti-oxidants.

The aforesaid organic resins to be used in the instant invention may be chosen from, but not limited to, acrylic, acrylic-urethane, epoxy, polyester, epoxy-polyester or fluorovinyl polymers. The resins may be a single resin or a combination of several resins that are designed to coat metal substrates for the purpose of corrosion protection.

The aforesaid organosulfur compounds that can be used as modifiers of the organic resins may be selected from but not limited to thiols, xanthates, alkyl sulfides, alkyl disulfides, thiocarbamates, dithiocarbamates, thioureas, thiophenols, mercaptopyridines, mercaptoanilines, mercaptoimidazoles, thiophenes, and thiophosphates. Moreover, bifunctional compounds with two terminal groups, one sulfur-containing and the other a non-sulfur containing polar group, can serve as

modifiers, provided that both groups are compatible with the afore said organic resins.

A distinguishing feature of the instant invention is the simplicity in coating a metal surface with the modified-resins. There are no needs to add additional steps or equipment. A mixture of the resin and organosulfur compounds can be directly applied to a metal surface by any means that is usually employed for the original resin. Also, there are no needs to modify the procedures or equipment involved in curing the coated surface. In fact, the process as disclosed in the instant invention simplifies the process by eliminating the chromation step.

The aforesaid modified resin can contain 0.001–0.5 moles per liter (M) of organosulfur compounds, preferably in the range of 0.02–0.05 M. This concentration may be used for electrogalvanized steel. For other metals, the optimal concentrations may differ slightly.

The modified-resins can be applied to metal surfaces by a roll or a bar coater and be cured at a temperature in the range of 100–350°C. The coating thickness may be controlled according to the needs. For galvanized steels, coating thickness in the range of 1-2 μm may be sufficient as conversion coatings for cold-rolled steels.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate an embodiment of the invention, and, together with the description, serve to explain the principles of the invention:

Figure 1 shows the photographs of the EG steel panels after 250 hours of salt spray tests. The unprotected panel showed red rust, while the EG steel coated with unmodified resin shows white rust. The panel coated with a resin containing 1-octadecanthiol (ODT) shows no sign of rust.

Figure 2 is a schematic illustration of a metal substrate coated with a resin that has been modified with an organosulfur compound. The triangles, squares and circles represent the components of the polymer. The rods represent the organosulfur modifier.

Figure 3 shows the hotographs of the EG steel panels after 144 hours of salt spray tests. The unprotected EG steel showed red rust, while the panel coated with unmodified resin shows signs of corrosion. The EG steel coated with a resin containing 16-mercaptohexadecanoic acid (MCA) shows no sign of corrosion.

Figure 4 shows the photographs of the EG steel panels after 168 hours of salt spray tests. The panels were coated with i) resin alone, ii) resin mixed with ODT dissolved in ethanol, iii) resin mixed with ODT dissolved in 1-butanol, and iv) resin mixed with ODT in 1:1 blend of ethanol and 1-butanol. All ODT solutions were at 0.1 M, and the resin and ODT solutions were blended at 70:30 ratio by volume.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferred embodiment of the present invention will hereinafter be described in detail with reference to the accompanying drawings.

According to the instant invention, four steps are involved to coat a metal substrate with the aforesaid modified resin. First, a solution of organosulfur compound is prepared with a proper solvent. A separate resin solution is also prepared according to the prescribed procedure for a particular resin. Second, the solution of the organosulfur compound is mixed with the resin solution at an optimal ratio. Third, the mixed solution is then applied to a metal surface by means of a suitable coating technique, for example, rolling, dipping, brushing, and spraying. Fourth, the coating is cured at an appropriate temperature to solidify the film on the metal substrate. As an alternative to steps one and two above, the organosulfur compound may be directly dissolved into the resin solution.

The organosulfur compounds that can be used for modifying resins may be selected from thiols, xanthates, alkyl sulfides, alkyl disulfides, thiocarbamates, dithiocarbamates, thioureas, thiophenols, mercaptopyridines, mercaptoanilines, mercaptoimidazoles, thiophenes, and thiophosphates. These reagents can be of alkyl or aryl compounds, but straight chain alkyl compounds are preferred. Moreover bifunctional compounds with two terminal groups, one sulfur-containing and the other non-sulfur containing polar group, can serve as modifiers, provided that both groups are compatible with the resin.

It should be understood that a proper solvent has to be chosen to make the solution of organosulfur compound compatible with the resin solution. The compatibility may mean that both solutions are miscible when mixed together, and a mixture of both solutions can produce a satisfactory coating without defects. A proper solvent should be chosen so that the aforesaid resin-organosulfur mixture can remain stable for a desired period of time and also have a suitable fluidity. Of course, the solvents should be environmentally acceptable and have a pleasant odor. The

preferred solvents include, but are not necessarily limited to, alcohols, acetone, turpentine, benzene, ethyl and butyl acetate, toluene, petroleum ester, xylene, alkane, mineral spirit, and water. The particularly preferred solvents of the present invention are ethanol, 1-propanol, 1-butanol, or their mixture.

5 Another critical aspect of the invention is the mixing ratio between the solutions of the resin and the modifier. The mixing ratio controls the concentration of modifier in the resin-organosulfur mixture. In a preferred embodiment, the concentration of the modifier in the mixture can be in the range of 0.001–0.5 M, preferably in the range of 0.02–0.05 M.

10 Another feature of the instant invention is that the modifiers can be added to a paint, which is a blended resin mixture containing one or more additional additives such as a pigment and a filler.

The modified resin of the invention can provide corrosion resistance in a variety of metal substrates including, but not limited to, hot rolled and pickled steel sheet, CRS sheets, stainless steel sheet, hot-dipped metallic coated steel sheets, 15 electroplated metallic coated steel sheets, aluminum sheets and aluminum alloy sheets, zinc sheets, zinc alloy sheets, copper sheets, copper alloy sheets, gold, and silver. The metallic coating may include one or more layers of lead, lead alloy, nickel, nickel alloy, zinc, zinc layer, tin, tin alloy, and the like. A phosphate conversion coating may also be applied to these steel sheets prior to being coated with the resin-organosulfur 20 mixture. The metal substrates may include continuous strip and foil, sheets cut to lengths as well as bars, angles, tubes and beams.

As depicted in Fig. 2, the organosulfur modifier may chemically bind with metal surface and, therefore, enhance the adhesion between the coating and substrate, 25 giving an improved resistance to chemical attack, mechanical stress and weathering. The small organosulfur molecules may also fill the pores present in the matrix of resin and help reduce the diffusion rate of corrosive media such as water, oxygen and ions to metal surface. Another effect of the additives is that organosulfur molecules can orient over the topmost surface of the resin coating where the terminal groups of the 30 surfactant may protrude. The orientation of organosulfur molecules over the topmost surface may be such that the coating has a lower surface free energy and act as the first protection against attack by corrosive media. The organosulfur compounds may also serve as anti-oxidants. The modified resin coating can significantly improve

corrosion resistance when compared with pure resin coatings because of synergistic effects between the organosulfur compounds and the cured resin.

In a preferred embodiment, the organosulfur compound used as a modifier of a resin to form a protective coating on metal surface comprise an alkanethiol having the general formula $R(CH_2)_nSH$, where R is a terminal group, which can be, but not necessarily limited to. H-, NH_2 -, $HOOC$ -, HO-. The number n represents the length of hydrocarbon chain, which can range from 7 to 21, and is most preferably 10 and 18. A particularly preferred embodiment of the present invention is 1-octadecanethiol (ODT, $CH_3(CH_2)_{17}SH$). Details of a blended resin-organosulfur mixture of the invention will be better understood from the following examples.

Example 1

A 0.1-M ODT solution was prepared in ethanol. The resin solution was prepared by mixing 99 parts of polymer solution and 1 part of inorganic hardener solution, both of which were provided by a chemical company. The ODT solution and resin solution were subsequently mixed together in the ratio of 30:70 by volume. The resultant mixture solution was applied to a test panel of 12×7.5 cm by means of a No. 5 bar coater. The panel was an electrogalvanized (EG) CRS sheet from Pohang Iron and Steel Company (POSCO). The coated panel was then cured in an oven at a temperature of $150^\circ C$ for 5 minutes. As a result, a uniform, lightly gray-colored coating was formed on the steel panel with thicknesses in the range of 1-2 μm . For comparison, another EG steel panel was coated with the aforesaid resin solution without ODT. The test panels coated with the resins with and without ODT were subjected to salt spray test (SST) by following the test procedures of ASMT B117. Also subjected to SST was another EG steel panel without any treatment (control).

Figure 1 shows the photographs of the three test panels after 250 hours of salt spray tests. White rusts appeared on the surface of the control panel after 2-4 hours, while the resin coated panel showed white rusts after 48-72 hours. In contrast, the EG steel panels that had been coated with ODT-modified resin remained rust free after 250 hours of SST. The water beads present in the surface indicate that the surface was still hydrophobic and still remained resistant to the attack of salt fogs. This example demonstrated that the corrosion resistance of resin coating on EG steel sheets can be improved by at least three times with the addition of ODT.

Example 2

This example illustrates the optimization of the concentration of ODT as a modifier in the resin. The coatings of ODT-modified resins were prepared in the same manner as described in Example 1, but the mixing ratio between resin solution and ODT solution (0.1M in ethanol) was varied in the range of 90:10 to 40:60 by volume. The EG steel panels coated with the ODT-modified resins were subjected to salt spray tests.

For comparison, two other EG steel panels were also subjected to salt spray tests. One was without any treatment, and the other was coated with the unmodified resin. Still another panel was treated with chromate rinsing prior to coating it with the unmodified resin.

The results of the salt spray tests are given in Table 1. As shown, even a small amount of ODT added to the resin increased corrosion resistance considerably. As the ODT dosage was increased, the corrosion resistance was further increased. At very high dosages of ODT, the resistance decreased. It appears that the optimal mixing ratio between the resin solution and 0.1M ODT solution lies in the range of 70:30 and 60:40 by volume. Under the optimal conditions, the EG steel coated with ODT-modified resin were superior to the chrome-rinsed EG steel that had been coated with unmodified resin.

Table 1

The Results of the Salt Spray Tests Conducted on the EG Steel Panels Treated with Resins Containing Varying Amounts of 0.1 M ODT-in-Ethanol Solution

Test Panels and Treatment	Composition of Mixture		Initiation of White Rust in SST (hours)	Surface Free Energy (mJ/m ²)	Ranking
	Resin Solution (vol. %)	ODT Conc. (M)			
EG	--	--	2-4	45.25	9
EG+Resin	100	0	48-72	44.99	8
EG+Resin/ODT (90:10)	90	0.01	72-96	44.03	7
EG+Resin/ODT (80:20)	80	0.02	168-192	42.53	5
EG+Resin/ODT (70:30)	70	0.03	264-288	39.93	1
EG+Resin/ODT (60:40)	60	0.04	264-288	38.13	2
EG+Resin/ODT (50:50)	50	0.05	216-240	42.04	4

EG+Resin/ODT (40:60)	40	0.06	144-168	41.77	6
EG+Chrome+Resin	--	--	240-264	42.89	3

Also shown in Table 1 are surface free energies of the test panels. Interestingly, the corrosion resistance was maximum when the surface free energy of the coated surface was minimum. Thus, the improvement of corrosion resistance may be partially attributed to the decrease of surface free energy of the coating.

Table 2 shows the results of the Tafel studies conducted on the test panels coated with modified resins. As shown, the density of the corrosion current reaches a minimum at the optimal mixing ratios and, hence, at the maximum corrosion resistance. Thus, there was a clear correspondence between the results of the Tafel studies and the salt spray tests.

Table 2

Corrosion Currents of the EG Steel Panels Coated at Different Mixing Ratios between Resin and 0.1 M ODT-in-Ethanol Solutions

Treatment	Corrosion Current Density ($\mu\text{A}/\text{cm}^2$)	
	Before Soaking in 1 M NaCl solution	After Soaking in 1 M NaCl solution for 100 hours
EG+Resin	4.21	21.03
EG+Resin/ODT(90:10)	0.09	18.98
EG+Resin/ODT(80:20)	0.08	8.22
EG+Resin/ODT(70:30)	0.002	4.85
EG+Resin/ODT(60:40)	0.003	6.02
EG+Resin/ODT(50:50)	0.02	8.70
EG+Resin/ODT(40:60)	2.28	12.72

Example 3

In this example, a 16-mercaptohexadecenoic acid (MCA, $\text{HS}(\text{CH}_2)_{15}\text{COOH}$) was used instead of ODT as a resin modifier. This reagent was different from ODT in that it was a bi-functional sulfur-containing compound. A 0.025 M MCA solution was prepared with ethanol and then mixed with the resin solution at a ratio of 1:1 by volume, which was not necessarily the optimal mixing ratio. At this ratio, the resin-organosulfur mixture contained 0.0125 M MCA. The modified resin was used to coat

an EG steel panel with a No. 5 bar coater. The coated panel was cured at 150°C for 5 minutes. Under this condition, the coating thickness would be approximately 1-2 µm. The EG steel panel coated with the modified resin was subjected to salt spray test. For comparison, salt spray tests were also conducted on an uncoated EG steel panel and an EG steel panel that had been coated with the unmodified resin.

After 144 hours of salt spray tests, the untreated EG steel panel showed red rusts, while the panel coated with unmodified resin showed white rusts. On the other hand, the EG steel panel coated with the resin modified with MCA exhibited no sign of corrosion, as shown in Figure 3.

Example 4

In this example, ODT was dissolved in different solvents and mixed with the resin solution. The resin-ODT mixtures were used to coat EG steel panels, which were subsequently subjected to salt spray tests. The photographs of Figure 4 were taken after 168 hours of the salt spray test for the EG steel panels coated with the following:

- i) resin alone,
- ii) resin-ODT mix (70:30) with 0.1 M ODT-in-ethanol solution,
- iii) resin-ODT mix (70:30) with 0.1 M ODT-in-1-butanol solution;
- iv) resin-ODT mix (70:30) with 1:1 mixture of 0.1 M ODT-in-ethanol and 0.1 M ODT-in-1-butanol solution.

As shown in Figure 4, ODT-modified resin greatly increased the corrosion resistance of the EG steel. Both ethanol and 1-butanol served as satisfactory solvents for ODT. The resin-ODT mixtures exhibited low viscosities, but they were not very stable when ethanol was used as the solvent for ODT. 1-butanol was a better solvent for ODT and, hence, the resin-ODT mixture was more stable. However, the resin-ODT mixtures prepared with 1-butanol tended to be more viscous than the case of using ethanol as solvent. As a compromise, a blend of ethanol and 1-butanol provided stable resin-ODT mixtures with low viscosities. Other solvents may be used as solvents for ODT. It should also be noted here that when shorter-chain thiols are be used as resin modifiers, solvents of higher dielectric constants, including water, may be used.

While this invention has been described in connection with what is presently

considered to be the most practical and preferred embodiment, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

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